

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

JP 5-315806

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the nonaqueous electrolyte cell which uses carbonaceous material for a negative electrode, and its manufacture method.

[0002]

[Description of the Prior Art] For example, the nonaqueous electrolyte cell using the thing which to dissolve a lithium as a negative-electrode material and comes to dissolve an electrolyte in a non-aqueous solvent as the electrolytic solution has little self-discharge, operating potential is high, and it has the features, like shelf-life ability is excellent. For this reason, it is equal to prolonged use, and since it is reliable, it is widely used as a clock or various power supplies for memory backup, and is further observed also as a power supply of portable devices, such as a video camera, and small audio equipment, a microcomputer.

[0003] By the way, although a nonaqueous electrolyte cell has the thing of primary-cell specification in use, in order to use it as a power supply of portable devices, such as a video camera, including an above-mentioned nonaqueous electrolyte cell, when economical efficiency is taken into consideration, it is desirable that it is the rechargeable battery specification in which a recharge is possible, and still more nearly lightweight and to be large capacity are also desired. From such a point, as for the nonaqueous electrolyte cell, research and development are furthered towards large-capacity[rechargeable-battery-izing, lightweight-izing and]-izing.

[0004] as the nonaqueous electrolyte cell of rechargeable battery specification -- as negative-electrode material -- a lithium, a lithium alloy, or a lithium occluded substance -- as positive-electrode material -- MnO₂, TiS₂, MoO₃, MoS₂, V₂O₅, WO₃, and LiCoO₂ etc. -- what was used is proposed

[0005] especially the nonaqueous electrolyte rechargeable battery that used the lithium cobalt multiple oxide or the lithium nickel cobalt multiple oxide for the carbon material in which the dope and ** dope of a lithium are possible as a negative-electrode material as a positive-electrode material has high operating potential in it, and the high energy density is expected very much from a cycle performance being markedly alike and being excellent with *****, as compared with the nonaqueous electrolyte rechargeable battery which uses a metal lithium or a lithium alloy as a negative-electrode active material

[0006]

[Problem(s) to be Solved by the Invention] In the nonaqueous electrolyte rechargeable battery which uses the above carbonaceous material as a negative-electrode material by the way, as the electrolytic solution Usually, LiAsF₆, LiPF₆, LiBF₄, LiCF₃SO₃, LiCF₃CO₂, and the thing that comes to dissolve LiClO₄, are used for a non-aqueous solvent as an electrolyte. Among these [especially], it is LiAsF₆. LiPF₆ If the dissolved electrolytic solution is used, it is reported that good charge/discharge capability ability is obtained.

[0007] However, the nonaqueous electrolyte rechargeable battery which uses carbonaceous material as a negative-electrode material is LiAsF₆, LiPF₆, and LiBF₄ LiCF₃CO₂. If the dissolved electrolytic

solution is used, although charge/discharge capability ability will be obtained, when charge and discharge are repeated, there is a problem that capacity falls remarkably.

[0008] This is LiAsF₆ in the electrolytic solution, LiPF₆, LiBF₄, and LiCF₃ CO₂. It is found out that the amount of [the acid content which carries out shell isolation, especially] fluoric acid is the cause. That is, it is LiPF₆ as the electrolytic solution to the equivalent mixed liquor of propylene carbonate (PC) and 1 and 2 dimethoxyethane (DME). If the electrolytic solution which carried out 1 mol/l dissolution is saved at 45 degrees C, ten days after, the amount of [early] free acid will increase to 200 ppm at 2000 ppm. If the electrolytic solution the amount of this free acid increased is used for an above-mentioned cell and charge and discharge are performed to the bottom of a high temperature service, the dissolution of an active material and decomposition of the electrolytic solution will take place on the charge voltage beyond 4.10V, and the service capacity of a cell will fall remarkably.

[0009] In order that the amount of [in the electrolytic solution] isolation fluoric acid may react with the metal lithium of a negative electrode and it may generate lithium fluoride by the nonaqueous electrolyte cell which uses a metal lithium as a negative electrode, there is no ***** especially in a cell performance about influence. However, since the generation reaction of such a stable compound does not arise, the dissolution of an active material and decomposition of a non-aqueous solvent are caused, and cell capacity is made to fall remarkably as a result in the nonaqueous electrolyte rechargeable battery using carbonaceous material as a negative electrode. In order to prevent the fluoric acid isolation from an electrolyte, and to make an electrolyte exist in the electrolytic solution stably, the method of adding various additives is proposed. However, if an additive is added to the electrolytic solution, the influence of the cell performance on the additive itself will be large, and a satisfying property will not be acquired too.

[0010] Then, this invention is proposed in view of this conventional actual condition, and the stability of the electrolytic solution is high and it aims at offering the nonaqueous electrolyte cell excellent in the charge-and-discharge cycle performance.

[0011]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the nonaqueous electrolyte cell of this invention is characterized by the amount of [of the above-mentioned nonaqueous electrolyte] free acid being 100 ppm or less in the nonaqueous electrolyte cell which comes to have the negative electrode which consists of carbonaceous material in which the dope and ** dope of a lithium are possible, a positive electrode, and nonaqueous electrolyte which comes to dissolve an electrolyte in a non-aqueous solvent.

[0012] Moreover, after it faces the manufacture method of this invention preparing nonaqueous electrolyte and it dissolves an electrolyte in a non-aqueous solvent, it is characterized by removing a part for a free acid according to chemisorption or a chemical reaction.

[0013] By the nonaqueous electrolyte cell of this invention, carbonaceous material is used as a negative-electrode material. The nonaqueous electrolyte cell which uses carbonaceous material as a negative-electrode material is LiAsF₆, LiPF₆, LiBF₄, and LiCF₃ CO₂. When the dissolved electrolytic solution is used, good charge/discharge capability ability is demonstrated. However, since fluoric acid is isolated from an electrolyte, by this, such the electrolytic solution induces the dissolution of an active material and decomposition of a non-aqueous solvent, and cell capacity reduces it remarkably.

[0014] Then, in this invention, in order to prevent the fall of such a cell capacity, 100 ppm or less of free-acid part concentration of the electrolytic solution are preferably regulated to 50 ppm or less. By regulating a part for the free acid of the electrolytic solution to 100 ppm or less, the dissolution of the active material by isolation fluoric acid and decomposition of a non-aqueous solvent are suppressed, and a good charge-and-discharge cycle performance is demonstrated.

[0015] What is necessary is just to perform free-acid part removal processing to this electrolytic solution, after dissolving an electrolyte in a non-aqueous solvent, in order for the amount of free acid to prepare the electrolytic solution 100 ppm or less.

[0016] Although there are a method of making the amount of free acid sticking to this chemisorption powder as free-acid part removal processing using the powder which chemisorbs a part for a free acid, a

method of making carry out the chemical reaction of the part for a free acid, and generating a compound, a way distillation removes a part for a free acid, etc., since there is almost no influence to an electrolyte while operation is easy, the method using chemisorption powder is suitable. That is, by the method of generating a compound, in order for the chemisorption matter etc. to have to remove a generation compound finally, there are many processes, operation is complicated and there is a possibility that the property of the electrolytic solution may deteriorate [an electrolyte] under a high temperature service since it is unstable, by the method using distillation.

[0017] In the method using chemisorption powder, the impalpable powder of aluminum $2O_3$, BaO, MgO, activated carbon, a molecular sieve, a pulverization silicon dioxide, and various metallic oxides, the heat-treated acetylene black, and corks are used as chemisorption powder.

[0018] What is necessary is to fill up a column with chemisorption powder and just to make this column pass a solution, or it adds and stirs chemisorption powder in a solution and filters a solution after stirring, in order to remove a part for the free acid in a solution using these chemisorption powder for example.

[0019] In addition, although carbon materials, such as conductive polymer, such as a polyacetylene and polypyrrole, or corks, polymer charcoal, and a carbon fiber, can be used for the carbonaceous material used as a negative-electrode material in the above-mentioned nonaqueous electrolyte cell, it is desirable to use carbonaceous material from the point that the energy density per unit volume is large. As a carbonaceous material, pyrolytic carbons, corks, carbon black (petroleum coke, pitch coke, coal corks, etc.) (acetylene black etc.), a glassy carbon, an organic polymeric-materials baking object (what calcinated organic polymeric materials in the inert gas/air current or the vacuum at the suitable temperature of 500 degrees C or more), a carbon fiber, etc. are used.

[0020] On the other hand, as a positive-electrode material, manganese dioxide, a transition-metals oxide like a vanadium pentoxide, an iron sulfide, a transition-metals chalcogen ghost like a titanium sulfide, the conjugated compound of these and a lithium, etc. can be used. Since the high voltage and high-energy density are obtained and it excels also in a cycle property especially, a lithium cobalt multiple oxide and a lithium cobalt nickel multiple oxide are desirable.

[0021] Especially as an organic solvent used for the electrolytic solution, although not limited, independent or two or more sorts of mixed solvents, such as propylene carbonate, ethylene carbonate, butylene carbonate, gamma butyl lactone, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, the 4-methyl -1, 3-dioxolane, jig limes, TORIGU limes, a sulfolane, a dimethyl carbonate, diethyl carbonate, and a carbonic acid dipropyl, can be used.

[0022]

[Function] In this invention, the free-acid part concentration of the electrolytic solution is low stopped with 100 ppm or less in the nonaqueous electrolyte cell which uses carbonaceous material for negative-electrode material. By the nonaqueous electrolyte cell which uses many [for a free acid] electrolytic solution, the metal component of the active material which exists in the electrolytic solution is in the state of being easy to trigger the lytic reaction by high potential, a metal component corrodes and dissolves easily by the operation for a free acid, and the capacity fall accompanying a charge-and-discharge cycle is large.

[0023] By the nonaqueous electrolyte cell for which free-acid part concentration uses the electrolytic solution 100 ppm or less, since the capacity fall caused by the amount of such free acid is prevented, a good charge-and-discharge cycle property is demonstrated. In addition, for free-acid part concentration, the electrolytic solution 100 ppm or less is aluminum $2O_3$ about an electrolytic solution. By making powder etc. contact, the amount of free acid is made to stick to this powder chemically, and it is easily prepared by removing.

[0024]

[Example] Hereafter, the concrete example of this invention is explained based on an experimental result.

[0025] The composition of the nonaqueous electrolyte cell produced by example 1 this example is

shown in drawing 1.

[0026] First, the negative electrode 1 was produced as follows. After carrying out introduction (the so-called oxygen bridge formation) of the functional group which contains oxygen in this 10 to 20%, using a petroleum pitch as a start raw material, it heat-treated at 1000 degrees C among the inert gas air current, and the carbon material with the property near a glassy carbon was obtained. As a result of performing X diffraction measurement about this carbon material, the spacing of a field (002) was 3.76Å. This carbon material was ground and it considered as the carbon-material powder of 10 micrometers of mean particle diameters.

[0027] thus, the polyvinylidene-fluoride (PVDF) 10 weight section which makes the obtained carbon-material powder a negative-electrode active material, and serves as this carbon-material powder 90 weight section and a binder -- mixing -- a negative electrode -- the mixture was prepared this negative electrode -- the N-methyl-2-pyrrolidone used as a solvent was made to distribute a mixture, and it was made the shape of a slurry and this negative electrode -- a mixture -- after applying the slurry to both sides of band-like copper foil with a thickness of 10 micrometers it is thin to the negative-electrode charge collector 9 uniformly and making them dry it, it pressed with the roll-press machine and the band-like negative electrode 1 was produced

[0028] Next, the positive electrode 2 was produced as follows. The positive active material (LiCoO_2) mixed one mol of cobalt carbonate with 0.5 mols of lithium carbonates, and calcinated and obtained it in 5-hour air at 900 degrees C. the polyvinylidene-fluoride 3 weight section used as this LiCoO_2 90 weight section and binder -- mixing -- a positive electrode -- the mixture was prepared this positive electrode -- the N-methyl-2-pyrrolidone used as a solvent was made to distribute a mixture, and it considered as the shape of a slurry this positive electrode -- a mixture -- after applying the slurry to both sides of a band-like aluminum foil with a thickness of 20 micrometers it is thin to the positive-electrode charge collector 10 uniformly and making them dry it, it pressed with the roll-press machine and the band-like positive electrode 2 was produced

[0029] The swirl formula electrode element as shown in drawing 1 was produced by carrying out the laminating of the separator 3 which consists of the band-like negative electrode 1, the band-like positive electrode 2, and a microporosity polypropylene film with a thickness of 25 micrometers to the sequence of a negative electrode 1, separator 3, a positive electrode 2, and separator 3, and winding this layered product around a swirl object many times.

[0030] Thus, the produced swirl formula electrode element was contained in the iron container 5 which performed nickel plating. The electric insulating plate 4 has been arranged to swirl formula electrode element vertical both sides, and the positive-electrode lead 12 made from aluminum was drawn from the positive-electrode charge collector 10, and the negative-electrode lead 11 made from nickel was drawn on the cell lid 7 from the negative-electrode charge collector 9, and it welded to it at the cell can 5.

[0031] Next, the electrolytic solution poured in into a cell can was prepared as follows. It is LiPF_6 in the solvent which mixed (propylene carbonate PC) 50 capacity % and 1 and 2-dimethoxyethane (DME) 50 capacity %. 1 mol/l dissolution was carried out. And the column with which the BaO powder which dried this solution was filled up was passed, and free-acid part concentration was measured.

[0032] In order to have measured free-acid part concentration, 10g of samples was first weighed precisely in the stoppered flask using the analytical balance in the dry box (moisture of 100 ppm or less), and it isolated preparatively. Subsequently, the cold water mixed so that it might become the rate which ice:distilled water becomes 50:50 beforehand was added to the above-mentioned sample, it was referred to as 100ml, 20g of bromthymol-blue powder was further added as an indicator, and solution temperature was made into 0-5 degrees C. And it asked for the point of neutralization about this solution using N / 10NaOH solutions with which Factor F is searched for beforehand. In addition, the terminal point was made into the point which changed to the purple-blue color from orange, and the purple-blue color maintained for 5 seconds. Based on the following formulas, acid-content concentration was calculated from the called-for point of neutralization.

[0033] $C = (0.002 \times A \times F / S) \times 100A$: Point of neutralization (ml)

C: Acid-content concentration (% of the weight)

F: The factor FS of NaOH : sample weight (g)

Consequently, the acid-content concentration of the above-mentioned electrolytic solution was 30 ppm. [0034] Thus, the prepared electrolytic solution was poured in into the cell can, the cell lid 7 was fixed by closing the cell can 5 through the insulating obturation gasket 6 which applied asphalt, and the cylinder nonaqueous electrolyte cell (example cell 1) with a diameter [of 20mm] and a height of 50mm was produced.

[0035] And about the produced cell, it charged on condition that upper limit voltage 4.1V, and carried out for charging current 1A, and charging-time 2.5 hours by repeating 6 ohms of resistance, and the charge-and-discharge cycle which discharges on condition that final-voltage 2.5V. And the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0036] It faces preparing the example 2 electrolytic solution, and is LiPF₆ in the mixed solvent of PC50 capacity % and DME50 capacity %. 1 mol/l dissolution was carried out, the electrolytic solution was prepared, and the nonaqueous electrolyte cell (example cell 2) was produced like the example 1 except having passed the packed column of dryness MgO powder for this electrolytic solution. In addition, the amount of [of the prepared electrolytic solution] free acid was 45 ppm.

[0037] It carried out by having repeated the charge-and-discharge cycle like [cell / nonaqueous electrolyte / which was produced] the example 1, and the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0038] It is LiPF₆ in the solvent which faced preparing the example 3 electrolytic solution and mixed L % of PC50 capacity, and DME50 capacity %. aluminum₂ O₃ which carried out 1 mol/l dissolution, prepared the electrolytic solution, and dried this electrolytic solution The powdered packed column was passed and the nonaqueous electrolyte cell (example cell 3) was produced like the example 1 except the lever. In addition, the amount of [of the prepared electrolytic solution] free acid was 35 ppm.

[0039] It carried out by having repeated the charge-and-discharge cycle like [cell / nonaqueous electrolyte / which was produced] the example 1, and the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0040] It is LiPF₆ in the solvent which faced preparing the example 4 electrolytic solution and mixed PC50 capacity % and DME50 capacity %. 1 mol/l dissolution was carried out, the electrolytic solution was prepared, and the nonaqueous electrolyte cell (example cell 4) was produced like the example 1 except having passed the packed column of the carbon (activated carbon) powder which dried this electrolytic solution. In addition, the amount of [of this electrolytic solution] free acid was 75 ppm.

[0041] It carried out by having repeated the charge-and-discharge cycle like [cell / nonaqueous electrolyte / which was produced] the example 1, and the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0042] It is LiBF₆ in the solvent which faced preparing the example 5 electrolytic solution and mixed PC50 capacity % and DME50 capacity %. aluminum₂ O₃ which carried out 1 mol/l dissolution, prepared the electrolytic solution, and dried this electrolytic solution The nonaqueous electrolyte cell (example cell 5) was produced like the example 1 except having passed the powdered packed column. In addition, the amount of [of this electrolytic solution] free acid was 30 ppm.

[0043] It carried out by having repeated the charge-and-discharge cycle like [cell / nonaqueous electrolyte / which was produced] the example 1, and the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0044] It is LiCF₃ CO₂ in the solvent which faced preparing the example 6 electrolytic solution and mixed PC50 capacity % and DME50 capacity %. aluminum₂ O₃ which carried out 1 mol/l dissolution, prepared the electrolytic solution, and dried this electrolytic solution The nonaqueous electrolyte cell (example cell 6) was produced like the example 1 except having passed the powdered packed column. In addition, the amount of [of this electrolytic solution] free acid was 60 ppm.

[0045] It carried out by having repeated the charge-and-discharge cycle like [cell / nonaqueous electrolyte / which was produced] the example 1, and the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0046] It is LiPF₆ in the solvent which faced preparing the example 7 electrolytic solution and mixed

PC50 capacity % and diethyl carbonate (DEC) 50 capacity %. aluminum₂O₃ which dissolved 1 mol [1 / l], prepared the electrolytic solution, and dried this electrolytic solution The nonaqueous electrolyte cell (example cell 7) was produced like the example 1 except having passed the powdered packed column. In addition, the amount of [of this electrolytic solution] free acid was 25 ppm.

[0047] Thus, it carried out by having repeated the charge-and-discharge cycle like [cell / nonaqueous electrolyte / which was produced] the example 1, and the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0048] It is LiPF₆ in the solvent which faced preparing the example of comparison 1 electrolytic solution, and mixed PC50 capacity % and DME50 capacity %. 1 mol/l dissolution was carried out and the nonaqueous electrolyte cell (example cell 1 of comparison) was produced like the example 1 except having used this electrolytic solution as the electrolytic solution as it was, without performing free-acid part removal processing. In addition, the amount of [of this electrolytic solution] free acid was 150 ppm.

[0049] Thus, it carried out by having repeated the charge-and-discharge cycle like [cell / nonaqueous electrolyte / which was produced] the example 1, and the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0050] It is LiPF₆ in the solvent which faced preparing the example of comparison 2 electrolytic solution, and mixed PC50 capacity % and diethyl carbonate (DEC) 50 capacity %. 1 mol/l dissolution was carried out and the nonaqueous electrolyte cell (example cell 2 of comparison) was produced like the example 1 except having used this electrolytic solution as the electrolytic solution as it was, without performing free-acid part removal processing. In addition, the amount of [of this electrolytic solution] free acid was 105 ppm.

[0051] Thus, it carried out by having repeated the charge-and-discharge cycle like [cell / nonaqueous electrolyte / which was produced] the example 1, and the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0052] It is LiPF₆ in the solvent which faced preparing the example of comparison 3 electrolytic solution, and mixed PC50 capacity % and diethyl carbonate (DEC) 50 capacity %. 1 mol/l dissolution was carried out, and after saving this electrolytic solution for six months in ordinary temperature, the nonaqueous electrolyte cell (example cell 3 of comparison) was produced like the example 1 except having used it as the electrolytic solution. In addition, the amount of [of this electrolytic solution] free acid was 250 ppm.

[0053] Thus, it carried out by having repeated the charge-and-discharge cycle like [cell / nonaqueous electrolyte / which was produced] the example 1, and the service capacity of 10 cycle eye and a 100 cycle eye was measured. The result is shown in Table 1.

[0054]

[Table 1]

	10サイクル目の 放電容量 S_{100} (mAh)	100 サイクル目の 放電容量 S_{10} (mAh)	容量保持率 S_{100} / S_{10} (%)
実施例電池 1	1 0 5 0	9 6 0	9 1. 4
実施例電池 2	1 0 4 5	9 5 0	9 0. 9
実施例電池 3	1 0 5 0	9 5 5	9 1. 0
実施例電池 4	1 0 4 0	9 0 0	8 6. 5
実施例電池 5	1 0 5 0	9 6 0	8 9. 4
実施例電池 6	1 0 4 5	9 1 0	8 7. 1
実施例電池 7	9 8 0	8 9 5	9 1. 3
比較例電池 1	1 0 3 0	7 3 0	7 0. 9
比較例電池 2	9 8 0	8 3 5	8 5. 2
比較例電池 3	9 8 0	7 7 5	7 9. 1

[0055] As shown in Table 1, in a nonaqueous electrolyte cell, the capacity fall accompanying a charge-and-discharge cycle in the free-acid part concentration of the electrolytic solution is small, and a **** cage, the example [part / for a free acid] cell 1 using the electrolytic solution 100 ppm or less - the example cell 7 have capacity retention (service capacity of the service capacity / 10 cycle eye of a 100 cycle eye) all as high as a low thing. Furthermore, as for the example [part / for a free acid] cell 1 using 50 ppm or less and the low electrolytic solution - the example cell 3, the example cell 6, and the example cell 7, capacity retention is 89% or more.

[0056] Therefore, in the nonaqueous electrolyte cell, this showed that it was effective to regulate electrolytic free-acid part concentration, when raising capacity retention.

[0057]

[Effect of the Invention] Since the free-acid part concentration of the electrolytic solution is low stopped with 100 ppm or less, in the nonaqueous electrolyte cell of this invention, the improvement in a charge-and-discharge cycle performance, elevated-temperature shelf-life ability, a self-discharge performance, the stability of the electrolytic solution, etc. is possible, so that clearly also from the above explanation. And the shelf-life ability of the electrolytic solution itself can also improve.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The nonaqueous electrolyte cell characterized by the amount of [of the above-mentioned nonaqueous electrolyte] free acid being 100 ppm or less in the nonaqueous electrolyte cell which comes to have the negative electrode which consists of carbonaceous material in which the dope and ** dope of a lithium are possible, a positive electrode, and nonaqueous electrolyte which comes to dissolve an electrolyte in a non-aqueous solvent.

[Claim 2] The manufacture method of the nonaqueous electrolyte cell characterized by removing a part for the free acid in this electrolytic solution according to chemisorption or a chemical reaction after facing preparing nonaqueous electrolyte, dissolving an electrolyte in a non-aqueous solvent and preparing an electrolytic solution.

[Translation done.]